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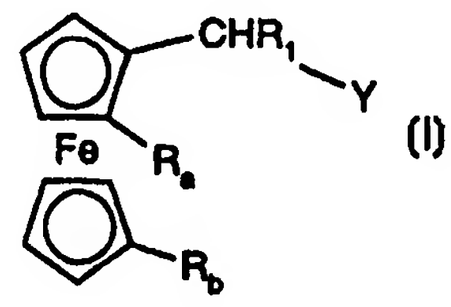
(54) Title: CHIRAL FERROCENYLS

(57) Abstract

The invention relates to chiral ferrocenyls of formula (I), wherein R_a is $-P(R_{10}R_{11})$ or $-SR_{12}$; R_b is $-P(R'_{10}R'_{11})$, $-SR'_{12}$, $-CH=NR_{12}$, $-CH_2-NH-R_{12}$ or $-CH_2-O-P(R_{10}R_{11})$; and the other substituents are as defined in claim 1, which may be used as ligands for transition metal catalysts in enantioselective reactions.



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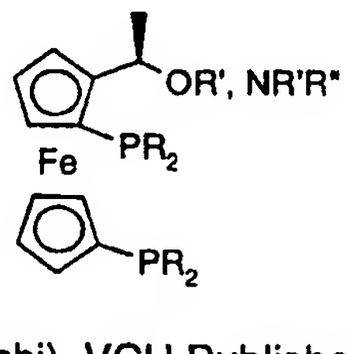
Chiral ferrocenyls

The invention relates to chiral ferrocenes substituted in the 1- and 1'-positions by two different radicals and also substituted in the 2-position, according to the general formula (I), to processes for their preparation and to the use thereof as ligands in catalysis.

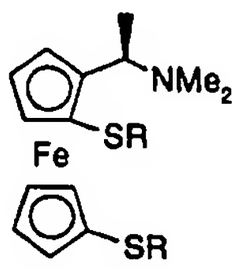
Metal complexes having chiral ferrocenyl ligands are known as catalysts for a number of reactions (e.g. enantioselective hydrogenation, hydrosilylation, formation of C-C bonds). The task of the chiral ligands is firstly so to adjust the electronic environment on the metal that a catalytic cycle becomes possible and secondly to transfer the chiral information to the substrate. Hitherto there has been no model that makes it possible to predict which chiral ligand will be best (especially in respect of enantioselectivity) for the catalytic reaction of a substrate. It is therefore advantageous if the electronic and steric properties of a ligand can be coordinated within a wide range both roughly and precisely.

Most of the diphosphine ligands described hitherto, however, contain two identical phosphines. That applies also to the chiral ferrocenyl ligands described by T. Hayashi *et al.* which have already been used successfully in a large number of catalytic reactions. Those ligands correspond, for example, to the following formula:

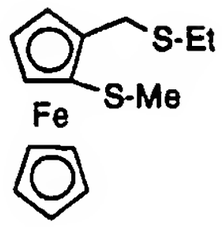


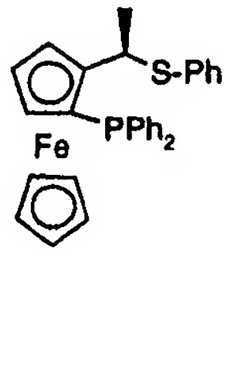
and are described in T.Hayashi, Ferrocenes (Ed.: A. Togni and T. Hayashi), VCH Publishers New York (1995) 105-142.

Examples of chiral ferrocenyl ligands having at least one sulfur radical are:

(A) 

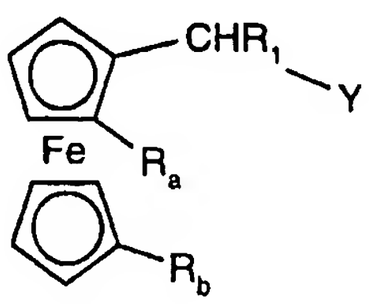
C.K. Lai, A.A. Naiini and C.H. Brubaker, Inorg. Chim. Acta, 164 (1989) 205-10.

(B)  C.H. Wang and C.H. Brubaker, J. Mol. Catal., 75 (1992) 221-33.

(C)  Y. Nishibayashi, K. Segawa, J.D. Singh, S. Fukuzawa, K. Ohe and S. Uemura, Organometallics, 15 (1996) 370-9.

A synthesis method is described hereinbelow that for the first time makes it possible to prepare chiral ferrocenyl ligands selectively having two different radicals in the 1,1'-position. Preferably the two different radicals are two different phosphine radicals or sulfur radicals or a sulfur radical and a phosphine radical. This makes it possible to adjust the electronic and steric properties of the chiral ferrocenyls according to the invention and of their metal complexes within a very wide range.

The invention relates to compounds of the formula

 (I), wherein

R_1 is C_1-C_8alkyl, C_5-C_{12}cycloalkyl, phenyl or phenyl substituted by from 1 to 3 substituents selected from C_1-C_4alkyl and C_1-C_4alkoxy;

R_a is $-P(R_{10}R_{11})$ or $-SR_{12}$;

R_b is $-P(R'_{10}R'_{11})$, $-SR'_{12}$, $-CH=NR_{12}$, $-CH_2-NH-R_{12}$ or $-CH_2-O-P(R_{10}R_{11})$;

R_{10} and R_{11} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl; or

R_{10} and R_{11} together are C_4-C_8alkylene, C_4-C_8alkylene substituted by C_1-C_4alkyl or by phenyl, or annelated C_4-C_8alkylene;
R'_{10} and R'_{11} are each independently of the other as defined for R_{10} and R_{11} , with the proviso that -$P(R_{10}R_{11})$ is not identical to -$P(R'_{10}R'_{11})$;
R_{12} is H, C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, -$SiR_4R_5R_6$, halogen, -SO_3M, -CO_2M, -PO_3M, -NR_7R_8 , -$[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R'_{12} is as defined for R_{12} , with the proviso that -SR_{12} is not identical to -SR'_{12} ;
R_4, R_5 and R_6 are each independently of the others C_1-C_{12}alkyl or phenyl;
R_7 and R_8 are each independently of the other H, C_1-C_{12}alkyl or phenyl, or
R_7 and R_8 together are tetramethylene, pentamethylene or 3-oxa-1,5-pentylene,
R_9 is H or C_1-C_4alkyl;
M is H or an alkali metal;
X^- is the anion of an acid;
Y is -OR_{13} , -SR_{14} or -$NR_{15}R_{16}$;
R_{13} is H, C_1-C_{18}alkyl, -C(O)-C_{1-8}alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, -$SiR_4R_5R_6$, halogen, -SO_3M, -CO_2M, -PO_3M, -NR_7R_8 , -$[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R_{14} is H, C_1-C_{18}alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4-alkoxy, -$SiR_4R_5R_6$, halogen, -SO_3M, -CO_2M, -PO_3M, -NR_7R_8 , -$[^+NR_7R_8R_9]X^-$ and C_1-C_5- fluoroalkyl; and
R_{15} and R_{16} are each independently of the other C_1-C_{18}alkyl that may be substituted and/or interrupted by one or more hetero atoms, arylenes or carbocycles; or
-$NR_{15}R_{16}$ is a cyclic amine.

Preferred compounds of formula (I) are those in which R_a is -$P(R_{10}R_{11})$ and R_b is -$P(R'_{10}R'_{11})$, at least one substituent R_{10}, R'_{10}, R_{11} or R'_{11} having a chemical structure that is different from the other substituents; especially preferably R_{10} and R'_{10} and also R_{11} and R'_{11} have a different chemical structure from one another.

Examples of R_1 as alkyl are methyl, ethyl, n-propyl and isopropyl, n-butyl, isobutyl and tert-butyl, pentyl, hexyl, heptyl and octyl. Linear alkyl is preferred. It contains preferably from 1 to 4 carbon atoms. Methyl and ethyl are preferred, with methyl being especially preferred.

R_1 as cycloalkyl preferably contains from 5 to 8, especially 5 or 6, ring carbon atoms. Examples of cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl and cyclododecyl. Cyclopentyl and cyclohexyl are preferred, with cyclohexyl being especially preferred.

R_1 contains as substituted phenyl preferably 1 or 2 substituents. Alkyl substituents may be, for example, methyl, ethyl, n-propyl and isopropyl, n-butyl, isobutyl and tert-butyl, with methyl and ethyl being preferred. Alkoxy substituents may be, for example, methoxy, ethoxy, n-propoxy and isopropoxy, n-butoxy, isobutoxy and tert-butoxy, with methoxy and ethoxy being preferred. In a group of compounds of formula I, R_1 is preferably phenyl or phenyl substituted by 1 or 2 C_1-C_4alkyl or C_1-C_4alkoxy substituents.

R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, as alkyl may be linear or branched and contain preferably from 1 to 8, especially from 1 to 4, carbon atoms. Examples of that alkyl are methyl, ethyl, n-propyl and isopropyl, n-butyl, isobutyl and tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. Methyl, ethyl, n-propyl and isopropyl, n-butyl, isobutyl and tert-butyl are preferred. When R_{10} and R_{11}, and R'_{10} and R'_{11}, are identical, as alkyl they are especially isopropyl or tert-butyl.

R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, as substituted alkyl are derived from the above-mentioned alkyl, with alkyl having from 1 to 3 carbon atoms being especially preferred. Phenyl is preferred as substituent. Examples of that alkyl are benzyl, 1- and 2-ethylphenyl and n-propylphenyl and isopropylphenyl.

R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, as cycloalkyl preferably contain from 5 to 8, especially 5 or 6, ring carbon atoms. Examples of cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl and cyclododecyl. Cyclopentyl and cyclohexyl are preferred, with cyclohexyl being especially preferred.

The cycloalkyl may be substituted, for example by from 1 to 3 alkyl or alkoxy substituents. Examples of such substituents have been given above. Methyl and ethyl and methoxy and ethoxy are preferred. Examples of substituted cycloalkyl are methyl- and methoxy-cyclopentyl and -cyclohexyl.

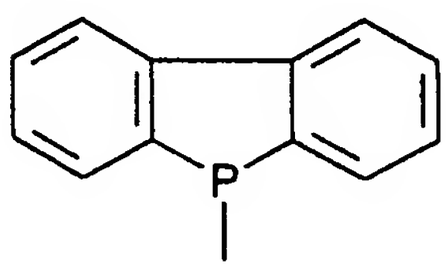
R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, as substituted phenyl preferably contain 1 or 2 substituents. When the phenyl contains 2 or 3 substituents, those substituents may be identical or different.

Examples of the substituents alkyl and alkoxy have been given above; preferred alkyl and alkoxy substituents for phenyl are methyl, ethyl and also methoxy and ethoxy.

When the phenyl substituent is halogen, it is preferably -F, -Cl or -Br.

When the phenyl substituent is C_1-C_5fluoroalkyl, it is wholly or partially fluorinated C_1-C_5alkyl. Examples thereof are the position isomers of mono- to deca-fluoropentyl, mono- to octa-fluorobutyl, mono- to hexa-fluoropropyl, mono- to tetra-fluoroethyl and mono- and di-fluoromethyl. Of the partially fluorinated alkyl radicals, those of the formulae $-CF_2H$ and $-CF_2(C_1$-C_4alkyl) are especially preferred. A perfluorinated alkyl is especially preferred. Examples thereof are perfluoropentyl, perfluorobutyl, perfluoropropyl, perfluoroethyl and especially trifluoromethyl. The fluoro-substituted alkyl groups are preferably bonded in the 3-, 4- and 5-positions.

When R_{10} and R_{11} together are C_4-C_8alkylene, C_4-C_8alkylene substituted by C_1-C_4alkyl or by phenyl, or annelated C_4-C_8alkylene, they are preferably a radical of formula IV, IVa, IVb or IVc



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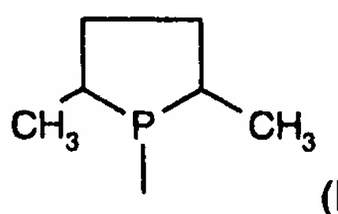

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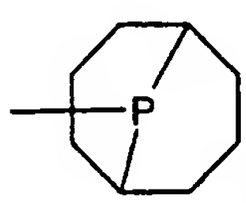

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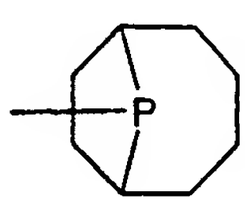


(IVc).

R_4, R_5 and R_6 may be linear or branched alkyl that preferably contains from 1 to 8, especially from 1 to 4, carbon atoms. Examples of alkyl have been given above. Preferred alkyl is methyl, ethyl, n-propyl, n-butyl and tert-butyl. Especially preferably the substituent $-SiR_4R_5R_6$ is trimethylsilyl.

Of the acidic phenyl substituents $-SO_3M$, $-CO_2M$ and $-PO_3M$, the groups $-SO_3M$ and $-CO_2M$ are preferred. M is preferably H, Li, Na or K.

R_7 and R_8 contain as alkyl preferably from 1 to 6, especially from 1 to 4, carbon atoms. The alkyl is preferably linear. Preferred examples are methyl, ethyl, n-propyl and n-butyl. R_9 as alkyl is preferably methyl.

X^- as an anion of an acid is preferably Cl^-, Br^- or the anion of a carboxylic acid, for example formate, acetate, trichloroacetate or trifluoroacetate, or BF_4^-, PF_6^- or SO_4^{2-} .

Preferred examples of R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, as substituted phenyl are 2-methyl-, 3-methyl-, 4-methyl-, 2- or 4-ethyl-, 2- or 4-isopropyl-, 2- or 4-tert-butyl-, 2-methoxy-, 3-methoxy-, 4-methoxy-, 2- or 4-ethoxy-, 4-trimethylsilyl-, 2- or 4-fluoro-, 2,4-difluoro-, 2- or 4-chloro-, 2,4-dichloro-, 2,4-dimethyl-, 3,5-dimethyl-, 2-methoxy-4-methyl-, 3,5-dimethyl-4-methoxy-, 3,5-dimethyl-4-(dimethylamino)-, 2- or 4-amino-, 2- or 4-methylamino-, 2- or 4-(dimethylamino)-, 2- or 4-SO_3H-, 2- or 4-SO_3Na-, 2- or 4-[$^+NH_3Cl^-$]-, 3,4,5-trimethyl-, 2,4,6-trimethyl-, 4-trifluoromethyl- and 3,5-di-(trifluoromethyl)-phen-1-yl.

Especially preferably R_{10}, R_{11} and R_{12}, and R'_{10}, R'_{11} and R'_{12}, are cyclohexyl, n-butyl, sec-butyl, tert-butyl, phenyl, 2- or 4-methylphen-1-yl, 2- or 4-methoxyphen-1-yl, 2- or 4-(dimethylamino)phen-1-yl, 3,5-dimethyl-4-(dimethylamino)phen-1-yl and 3,5-dimethyl-4-methoxyphen-1-yl, with cyclohexyl, phenyl, 4-methylphen-1-yl and n- and tert-butyl being especially preferred.

R_{13} and R_{14} may be as defined hereinbefore by way of example for alkyl and substituted phenyl. Preferably R_{13} and R_{14} are H, C_1-C_4alkyl or phenyl.

R_{15} and R_{16} may be linear or branched C_1-C_{18}alkyl analogously to the definitions given hereinbefore by way of example.

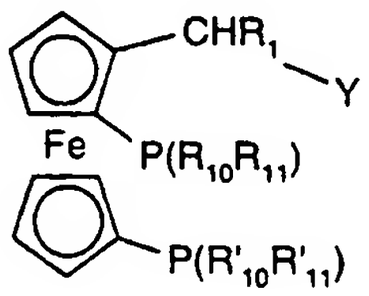
R_{15} and R_{16} as substituted alkyl may be C_1-C_{18}alkyl substituted by halogen, -OH, C_1-C_8alkoxy, aryloxy (such as phenyloxy or substituted phenyloxy), -SH, C_1-C_8alkylthio, arylthio (such as thiophenyl), $-NH_2$, primary or secondary C_1-C_8amine or by aryl (such as phenyl or naphthyl).

R_{15} and R_{16} as alkyl interrupted by one or more hetero atoms, arylenes or carbocycles may be alkyl comprising groups such as $-(CH_2CH_2O)-$, $-(CH_2CH_2CH_2O)-$, $-(CH_2CH_2S)-$, $-(CH_2CH_2CH_2S)-$, $-(CH_2CH_2NH)-$, $-(CH_2NHCH_2)-$, $-(CH_2N(C_1\text{-}C_8\text{alkyl})CH_2)-$, $-(CH_2(C_6H_4))-$ or $-(CH_2(C_6H_{10}))-$.

R_{15} and R_{16} as cyclic amine may be unsubstituted or substituted cyclic amines having a ring size of from 4 to 10, especially 5 or 6, atoms. Substituents are, for example, C_1-C_8alkyl or C_1-C_8alkylamine. In addition to the amine function, the ring may contain further hetero atoms, for example -O-, -S-, -NH- or -Nalkyl- .

Preferably Y is the group $-NR_{15}R_{16}$. Especially preferably $-NR_{15}R_{16}$ is $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N(n\text{-}C_3H_7)_2$, $-N(iso\text{-}C_3H_7)_2$, $-N(n\text{-}C_4H_9)_2$, pyrrolidyl, piperidyl, $-N(CH_3)CH_2C_3F_7$, $-N(CH_3)C_2H_4OH$, $-N(CH_3)C_2H_4OCH_3$, $-N(CH_3)CH(CH_2OH)_2$, $-N(CH_3)CH(CH_2OH)_2$, $-N(CH_3)C_2H_4N(CH_3)_2$, $-N(CH_3)C_2H_4N(CH_3)H$, $-N(CH_3)C_2H_4N(C_2H_5)_2$, $-N(C_2H_4OH)_2$, $-N(CH_3)C_2H_4N(C_5H_{10})$, $-N(CH_3)C_2H_4N(C_2H_4OC_2H_4)$ or $-N(CH_3)C_2H_4N(C_2H_4OC_2H_4OC_2H_4N(CH_3)C_2H_4OC_2H_4OC_2H_4)$.

Compounds of the formulae



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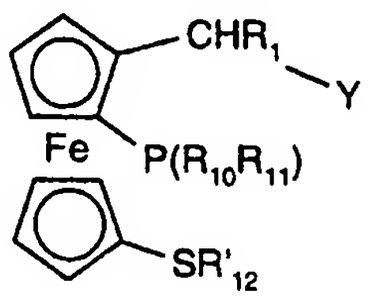

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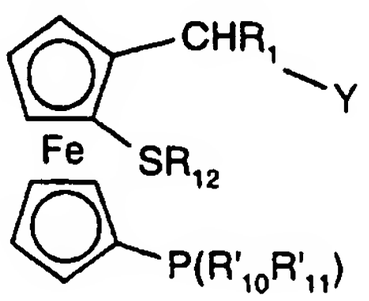
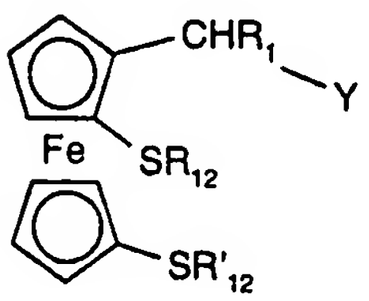
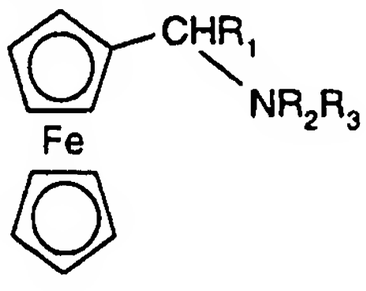


(Ic) and


(Id), wherein the substituents have the above-mentioned definitions and preferred meanings, are especially preferred.

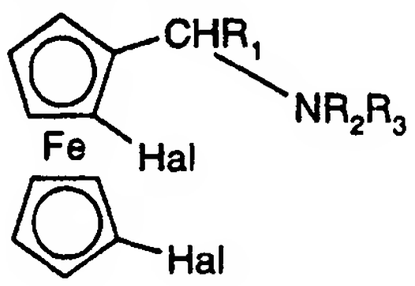
The compounds of formula (I) according to the invention can be obtained in accordance with the following process.

Starting from a compound of formula (II)



(II), wherein

R_1 is C_1-C_8alkyl, C_5-C_{12}cycloalkyl, phenyl or phenyl substituted by from 1 to 3 substituents selected from C_1-C_4alkyl and C_1-C_4alkoxy;
R_2 and R_3 are each independently of the other hydrogen or C_1-C_{12}alkyl;
that compound is reacted in an inert organic solvent first with one equivalent of alkyl-lithium and then, in the presence of an amine complexing agent for Li, with a second equivalent of alkyl-lithium, and the product is then reacted with a halogenating agent to form compounds of formula (III)



(III),

wherein Hal is F, Cl, Br or I.

R_2 and R_3 as alkyl may be linear or branched. Examples of C_1- to C_8-alkyl have been given above; additionally there may be mentioned the various isomers of nonyl, decyl, undecyl and dodecyl. R_2 and R_3 may also be bonded to one another and may form a cyclic alkyl group. Examples are pyrrolidine or piperidine.

Preferably R_2 and R_3 are each independently of the other methyl or ethyl; especially preferably they are both methyl.

An example of an amine complexing agent for Li is N,N,N,N-tetramethylethylenediamine.

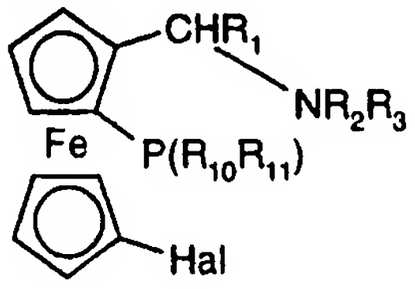
Within the context of this invention, alkyl-lithium is to be understood as being preferably tert-butyl-, sec-butyl- or n-butyl-lithium.

Halogenating agents are known in the general prior art for many reactions. For example, a number are mentioned in Gmelin, Handbuch der Anorganischen Chemie (Handbook of Inorganic Chemistry), Ferroorganic Compounds Part A Ferrocene 7, Eighth Edition, Springer Verlag 1980, pages 128-136.

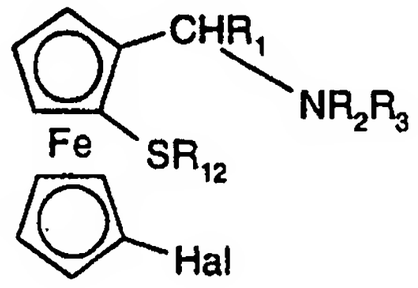
Preferably the halogenating agent is selected from the group consisting of Cl_2, hexachloroethane, 1,2-dichlorotetrafluoroethane, toluene-4-sulfonyl chloride, Br_2, 1,2-dibromotetrachloroethane, 1,2-dibromotetrafluoroethane, toluene-4-sulfonyl bromide, 2,3-

dimethyl-2,3-dibromobutane, I_2, 1,2-diiodotetrafluoroethane, perfluoropropyl iodide, perfluoroethyl iodide, toluene-4-sulfonyl iodide and perfluoromethyl iodide.

In a first step alkyl-lithium is added to the compounds of formula (III) in an inert organic solvent and allowed to react and then in a second step an organic solution of a compound of formula $ClP(R_{10}R_{11})$ (Va) or of formula $R_{12}SSR_{12}$ (Vb) is added, yielding compounds of formula



(VIa) or



(VIb), wherein R_{10}, R_{11} and R_{12} have the definitions and preferred meanings given above.

The substitution by the halogen atom takes place predominantly on the cyclopentadienyl ring that carries the second substituent (alkylamine).

The process is preferably carried out by adding alkyl-lithium at a temperature of from -90 to +30°C.

In the second step, the compounds of formula (Va) or (Vb) are preferably added at a temperature of from -90 to +30°C.

The compounds of formula (VIb) are novel and constitute a further aspect of this invention.

The compounds of formula (Ia) are obtainable by adding alkyl-lithium to compounds of formula (VIa), in an inert organic solvent, analogously to the above preparation process for the preparation of compounds of formula (VIa), causing the mixture to react and subsequently in a second step adding an organic solution of a compound of formula $ClP(R'_{10}R'_{11})$ (Vd), wherein R'_{10} and R'_{11} have the definitions and preferred meanings given above, and optionally converting the radical $-NR_2R_3$ into the radical -Y.

The compounds of formula (Ib) are obtainable by adding alkyl-lithium to compounds of formula (VIa), in an inert organic solvent, analogously to the above preparation process for the preparation of compounds of formula (VIb), causing the mixture to react and

subsequently reacting it with an organic solution of a compound of formula $R'_{12}SSR'_{12}$ (Vc), wherein R'_{12} has the definitions and preferred meanings given above, and optionally converting the radical $-NR_2R_3$ into the radical -Y.

Compounds having SR_{12} or SR'_{12} wherein R_{12} or R'_{12} is hydrogen can be prepared analogously to "Ferrocenes, Editors A. Togni and T. Hayashi, VCH Publishers 1995", pages 231-233.

The compounds of formulae (Ic) and (Id) are obtainable by adding alkyl-lithium to compounds of formula (VIb), in an inert organic solvent, analogously to the above preparation process for the preparation of compounds of formula (VIa) or (VIb), causing the mixture to react and subsequently reacting it with an organic solution of a compound of formula $ClP(R'_{10}R'_{11})$ (Vd) or of formula $R'_{12}SSR'_{12}$ (Vc), wherein R_{10}, R_{11} and R'_{12} have the definitions and preferred meanings given above, and optionally converting the radical $-NR_2R_3$ into the radical -Y.

The preparation of the compounds of formulae (I) and especially (Ia), (Ib), (Ic) and (Id) constitutes a further aspect of this invention.

The compounds of formula (I), (VIa) or (VIb) may be obtained in the form of racemates, pure enantiomers or mixtures of enantiomers. If the synthesis is carried out using enantiomerically pure compounds of formula (II) as starting materials, there are formed very preferentially only one of the two possible diastereoisomers of the compounds of formula (III) and consequently also of the compounds of formulae (VIa) and (VIb) and (I).

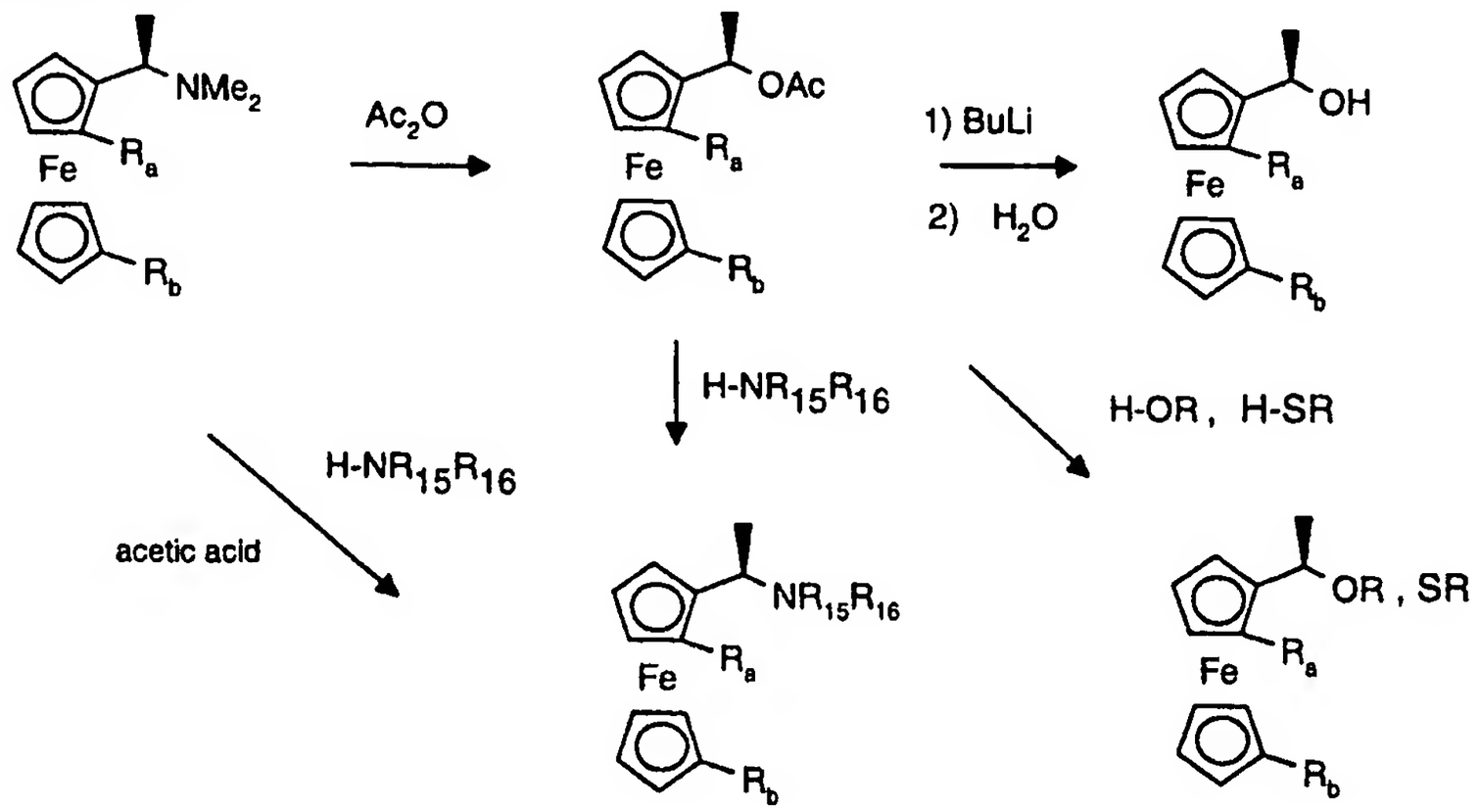
If racemates or optically active mixtures are used as starting materials, they can be separated into the stereoisomers by means of known methods, with chromatographic methods or crystallisation generally being preferred.

Isolation and purification of the compounds is carried out in accordance with methods known *per se*, for example distillation, extraction, crystallisation and/or chromatographic methods.

The compounds of formula (I) wherein R_b is $-CH=NR_{12}$ or $-CH_2-NH-R_{12}$ can be prepared starting from a compound of formula (VIa) or (VIb) by converting the halogen radical into a radical -CHO and subsequently reacting the product with a primary amine. The radical $-CH=NR_{12}$ can be converted into the radical $-CH_2-NH-R_{12}$ by further reaction with a reducing agent, such as $LiAlH_4$. The general reaction conditions are known to the person skilled in the art and may be generalized from the following Examples.

The compounds of formula (I) wherein R_b is $-CH_2-O-P(R_{10}R_{11})$ can be prepared starting from a compound of formula (VIa) or (VIb) by converting the halogen radical into a radical -CHO and subsequent reduction with a reducing agent, such as $LiAlH_4$, to form the alcohol, which is reacted with a chlorophosphine of formula $ClP(R_{10}R_{11})$. The general reaction conditions are known to the person skilled in the art and may be generalized from the following Examples.

To prepare further compounds of formulae (I) and especially (Ia), (Ib), (Ic) and (Id), the group NR_2R_3 can be converted into the various groups defined for Y in accordance with the following scheme.



Other alternative or subsequent process steps are known to the person skilled in the art.

A further aspect of this invention is constituted by transition metal complexes with ferrocenyl ligands of formula (I) and especially (Ia), (Ib), (Ic) or (Id). d^8-Transition metals, such as Rh, Ir, Ru, Pd, Ni and Au, are preferred, with Rh, Pd, Ni and Ir being especially preferred.

The transition metal complexes according to the invention can be used as catalysts, for example in hydrogenations, transfer hydrogenations and hydrosilylations of double bonds (C-C, C-O or C-N), allylic substitutions, hydroformylations or cross-coupling reactions. The individual, preferably enantioselective, catalytic reactions are known from the literature, for example, also with diphosphine ligands, and the catalysts according to the invention make it possible to vary the catalyst properties in a hitherto unknown manner by means of the two different ferrocenyl radicals. The widely differentiated electronic and steric environments that are thus possible on the transition metal make it possible to increase the stereo-selectivity, activity and/or productivity. A further aspect of this invention is accordingly the use of transition metal complexes containing a compound of formula (I), and especially (Ia), (Ib), (Ic) or (Id), in enantioselective catalysis.

The processes for the preparation of the transition metal complexes are analogous to those described in the literature and known to the person skilled in the art. The transition metal complexes are frequently prepared *in situ*, that is to say in the reaction medium in question. For example, in that process a ligand substitution by the ferrocenyls according to the invention is effected on the transition metal.

The definitions and preferred meanings for the individual substituents of the compounds of formula (I) and especially of formulae (Ia), (Ib), (Ic) and (Id) apply analogously also to the transition metal catalysts, to their preparation and to their use.

The following Examples illustrate the invention.

General process procedure:

All operations are carried out under an inert gas atmosphere (argon). Ether and THF are freshly distilled over sodium/benzophenone. Hexane and pentane are dried over a Pb/Na alloy. Unless specified to the contrary, Merck 60 silica gel is used as solid phase for the purification by chromatography.

Abbreviations used:

TMEDA: N,N,N,N-tetramethylethylenediamine

n-BuLi or BuLi: n-butyllithium (1.6 molar solution in hexane)

COD: 1,5-cyclooctadiene

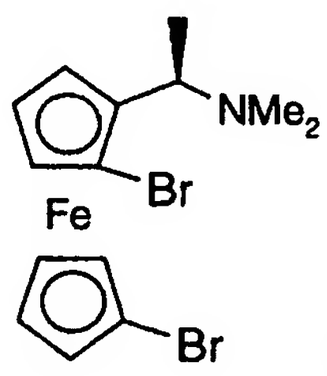
Cyh: cyclohexyl

o-Tol: o-tolyl

Tol: toluene
NBD: norbornadiene
Hex: hexane
Ph: phenyl
Me: methyl
Cyp: cyclopentyl
Cp: cyclopentadienyl
t-Bu: tert-butyl
Ac: acetyl

Example A2 Preparation of the compound of formula 2

(R)-N,N-Dimethyl-1-[(S)-1', 2 bis(bromo)-ferrocenyl]ethylamine



(2)

20.6 ml (33 mmol) of a 1.6M n-BuLi solution are added dropwise at room temperature, with stirring, to a solution of 7.71 g (30 mmol) of (R)-N,N-dimethyl-1-ferrocenylethylamine in 50 ml of diethyl ether. After 1.5 hours a further solution consisting of 22.5 ml (36 mmol) of a 1.6M BuLi solution in hexane and 4.95 ml (33 mmol) of TMEDA is added dropwise and the reaction mixture is stirred overnight. The dark-brown, cloudy reaction mixture is then cooled to from -72 to -78°C using a dry ice/isopropanol bath and, with stirring, 7.9 ml (66 mmol) of 1,2-dibromotetrafluoroethane are slowly added dropwise in such a manner that the temperature of the mixture does not exceed -74°C. The mixture is stirred for a further 1 hour with cooling and then for a further 2 hours without cooling. 50 ml of ice-water are added to the resulting orange suspension and extraction is carried out by shaking with 25 ml of ethyl acetate several times. The organic phases are collected, washed with water, dried with Na_2SO_4 and concentrated using a rotary evaporator. The brown crude product is purified by chromatography (silica gel: Merck 60; eluant: acetone). 7.5 g of compound 2 are obtained (yield 60%, brown oil).

Analysis:

^{1}H-NMR ($CDCl_3$): δ 1.53 (d, 3H, J = 7, C-CH_3), 2.13 (s, 6H, N(CH_3)$_2$), 3.78 (q, 1H, J = 7, CH-Me), 4.03-4.5 (m, 7H, $C_5H_3FeC_5H_4$).

Microanalysis calculated for $C_{14}H_{17}NBr_2Fe$: C, 40.52; H, 4.13; N, 3.38; Br, 38.51; Fe, 13.46.

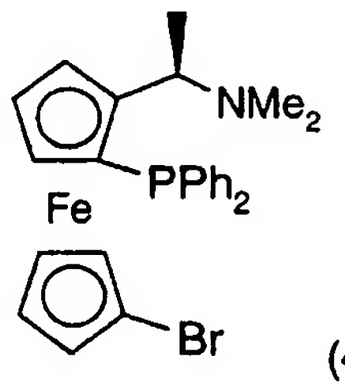
Found : C, 40.80; H, 4.10; N, 3.30; Br, 38.18.

Examples A4-A8:

The method is described using the example of compound (4). All the other compounds are prepared analogously. Different conditions and the results are given in Table 1.

Example A4 Preparation of the compound of formula 4

(R)-N,N-Dimethyl-1-[1'-(bromo), (S)-2-(diphenylphosphino) ferrocenyl]ethylamine



(4)

12.2 ml of a 1.6M BuLi solution in hexane (1 mmol of BuLi per mmol of starting material) are added dropwise at -30°C, with stirring, to a solution of 7.98 g (19.2 mmol) of compound (2) in 96 ml of diethyl ether (5 ml per mmol of starting material). The mixture is then cooled to from -78 to -70°C and 4.23 ml of Cl-PPh_2 (1.2 mmol of chloro-phosphine per mmol of starting material) are slowly added. The mixture is then allowed to warm to room temperature and is stirred for a further 2 hours. Water is then added to the resulting yellow suspension and extraction is carried out by shaking with hexane several times. The organic phases are collected, washed with water, dried with Na_2SO_4 and concentrated by rotary evaporation. The yellow-brown crude product is purified by chromatography (first, crude purification with silica gel: Merck 60; eluant: ethyl acetate, then chromatography over Alox; eluant toluene/hexane 1:10). 5.27 g of product are obtained (yield 53 %, orange-brown, almost solid).

The selectivity and yield of the reaction can be increased further if a nonpolar solvent is used. In pentane, instead of diethyl ether, a yield of more than 60% is obtained.
Analysis:
^{1}H-NMR ($CDCl_3$): δ 1.25 (d, 3H, J = 7, C-CH_3), 1.75 (s, 6H, N(CH_3)$_2$), 4.15 (m, 1H, J = 7, CH-Me), 3.7-4.4 (m, 7H, $C_5H_3FeC_5H_4$), 7.1-7.65 (m, 10H, P(C_6H_5)$_2$)
^{31}P-NMR ($CDCl_3$): δ -24.6

The optical purity can be verified by means of ^{1}H-NMR by the formation of a complex of (4) with di-μ-chloro-[(R)-dimethyl(α-methylbenzyl)aminato-C2-N]dipalladium(II) (*J. Chem. Soc., Dalton Trans., (1979) 2019*): no trace of the other enantiomer is observed.

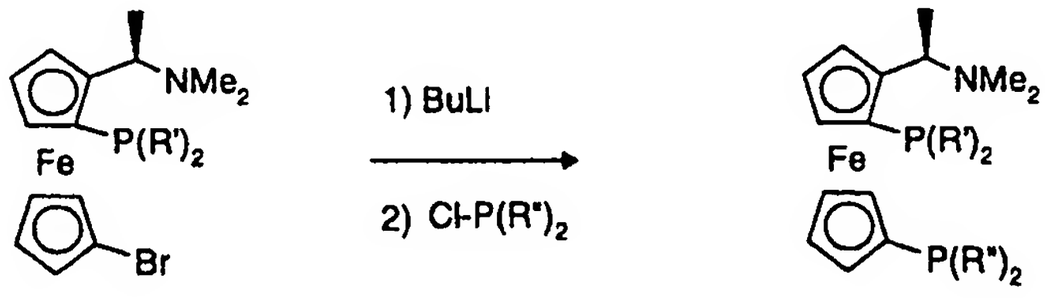
Table 1:

Comp. No.	R'	Amount mmol of start-ing mat.	Chromatogr. solid phase	Purification Eluant	Yield %	^{31}P δ	^{1}H δ NMe_2
4	Ph	19.2	1) Merck 60 2) Alox	ethyl acetate Tol 1/Hex 10	60	-24.6	1.75
5	Cyh	7.2	Merck 60	ethyl acetate	53	-11.8	2.1
6	Ph-p-CF_3	2.4	Alox	Hex	41	-24.1	1.74
7	Cyp	3.9	Merck 60	ethyl acetate 3/Hex 1	45	-20.2	2.1
8	o-Tol	7	Merck 60	ethyl acetate	58	-47.7	1.81

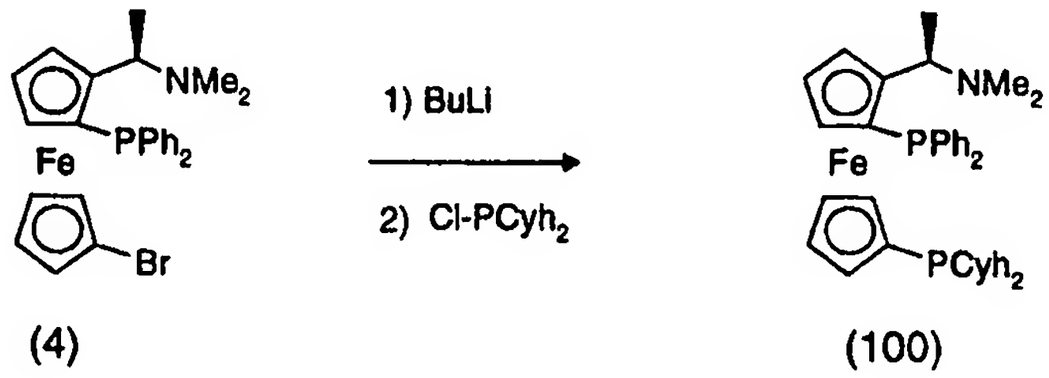
Diethyl ether is used as solvent except in the case of compound 4, when hexane is used.

Examples 1-11:

The method is described using the example of compound (100). All the other compounds are prepared analogously. Different conditions and the results are given in table form (see Table 2):



Example 1: Preparation of (R)-N,N-dimethyl-1-[1'-(dicyclohexylphosphino), (S)-2-(diphenylphosphino) ferrocenyl]ethylamine

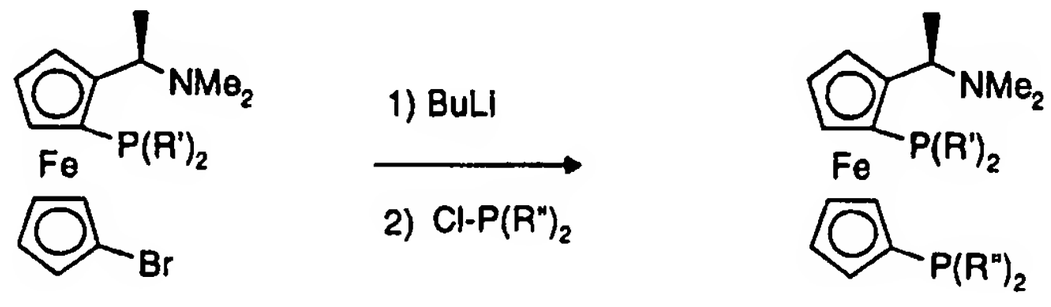


(4) (100)

2.16 ml of a 1.6M BuLi solution in hexane (1.2 mmol of BuLi per mmol of starting material) are added dropwise at -30°C, with stirring, to a solution of 1.5 g (2.88 mmol) of (4) in 20 ml of diethyl ether (7 ml per mmol of starting material). The mixture is then cooled to from -78 to -70°C and 0.84 g of chloro-dicyclohexylphosphine (1.25 mmol of chloro-phosphine per mmol of starting material) is slowly added. The mixture is then allowed to warm to room temperature and is stirred for a further 2 hours. Water is then added to the resulting yellow suspension and extraction is carried out by shaking with ethyl acetate several times. The organic phases are collected, washed with water, dried with Na_2SO_4 and concentrated by rotary evaporation. The yellow-brown crude product is purified by chromatography (silica gel: Merck 60; eluant: ethyl acetate/hexane 1/3). 1.33 g of product are obtained (yield 72.5 %, orange powder).

^{31}P-NMR ($CDCl_3$): δ -8.1 ($PCyh_2$), -23.4 (PPh_2)

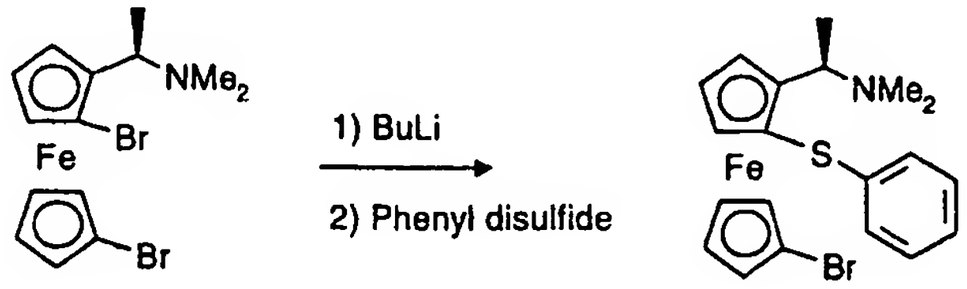
Table 2: Synthesis of the diphosphine compounds:



Comp. No.	R'	R"	Start-ing mat. Ex. No.	Amount mmol of start-ing mat.	Purification Eluant	Yield %	^{31}P $\delta PR'_2$	^{31}P $\delta PR"_2$
100	Ph	Cyh	A4	2.9	ethyl acetate 1/Hex 3	73	-23.4	-8.1
101	Ph	Cyp	A4	1.76	ethyl acetate 1/Hex 3	57	-23.2	-11.3
102	Ph	o-Tol	A4	2.9	ethyl acetate 1/Tol 2	30	-23.6	-37.6
103	Ph	Ph-p-CF_3	A4	0.58	ethyl acetate 1/Hex 1	30	-24.1	-17.1
104	Cyh	Ph	A5	0.3	ethyl acetate 1/Hex 8	54	-11.4	-18.0
105	Ph-p-CF_3	Cyh	A6	0.29	Hex	47	-22.7	-8.5
106	Ph-p-CF_3	Ph	A6	0.46	ethyl acetate 1/Tol 10	40	-23.0	-18.0
107	Ph-p-CF_3	t-Bu	A6	0.46	ethyl acetate 1/Hex 2	62	-22.9	+26.8
108	Cyp	Ph	A7	0.71	ethyl acetate 1/MeCl 1	84	-20.4	-17.6
109	o-Tol	Cyh	A8	2.1	ethyl acetate, 0.5 % NEt_3	82	-45.0	-6.2
110	o-Tol	Ph	A8	2.0	ethyl acetate, 0.5 % NEt_3	73	-45.4	-16.1

Merck 60 silica gel is used as the solid phase except in the case of compound 105, when Alox is used.

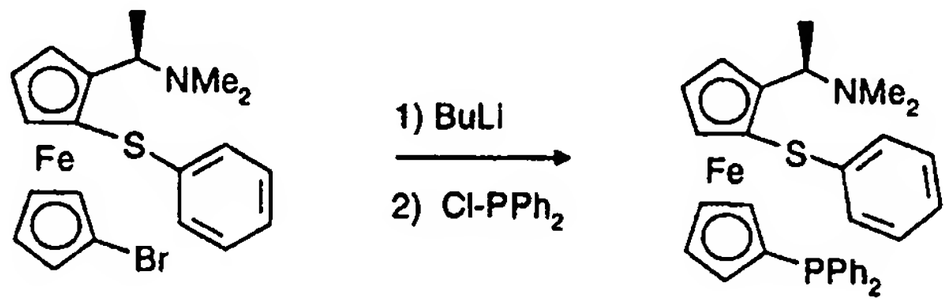
Example 12:



(2) (10)

4.97 ml (7.95 mmol) of BuLi are added dropwise at approximately -40°C over a period of 30 minutes to a solution of 3 g (7.23 mmol) of compound (2) in 42 ml of pentane, and the mixture is stirred at that temperature for a further 30 minutes. The mixture is then cooled to -78°C and 2.05 g (9.4 mmol) of phenyl disulfide are added, cooling is removed and the mixture is stirred overnight. Saturated sodium hydrogen carbonate solution is then added to the reaction mixture and extraction is carried out 3 times with ethyl acetate. The combined organic phases are washed with saturated NaCl solution, dried over sodium sulfate, concentrated by rotary evaporation and purified by chromatography (first, silica gel: Merck 60; eluant: acetone, then Alox III; eluant: hexane / 0.5% triethylamine). 1.41 g of product (100) are obtained (yield 44%, yellow powder).

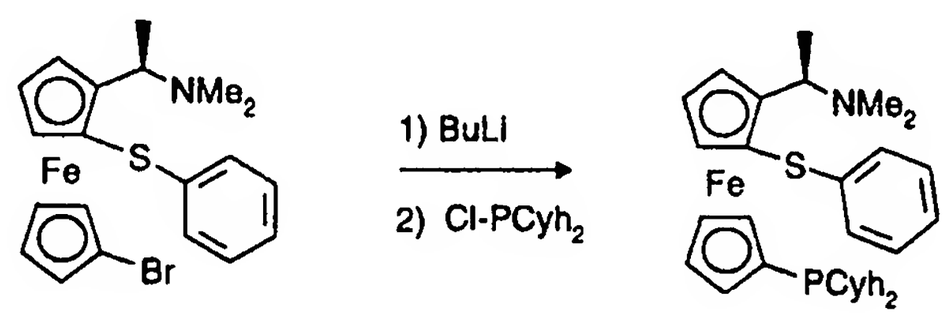
Example 13:



(10) (111)

0.93 ml (1.49 mmol) of BuLi is added dropwise at approximately -40°C to a solution of 600 mg (1.35 mmol) of compound (10) in 5 ml of diethyl ether, and the mixture is stirred at that temperature for a further 30 minutes. The mixture is then cooled to -78°C and 0.33 ml (1.76 mmol) of chloro-diphenylphosphine is added, cooling is removed and the mixture is stirred overnight. Water is then added to the reaction mixture and extraction is carried out 3 times with ethyl acetate. The combined organic phases are washed with saturated NaCl solution, dried over sodium sulfate, concentrated by rotary evaporation and purified by chromatography (silica gel: Merck 60; eluant: acetone). 0.72 g of product is obtained (yield 97 %, orange oil).

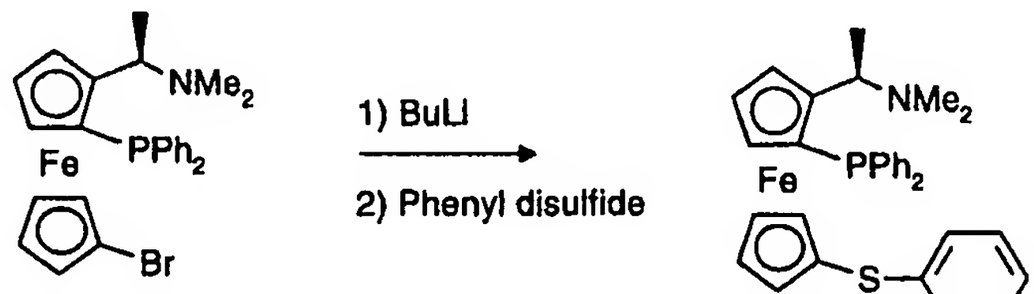
Example 14:



(10) (113)

Starting with 600 mg of compound (10), compound (113) is prepared in nalogy to compound (111). 0.63 g of product is obtained (yield 83 %, orange oil).

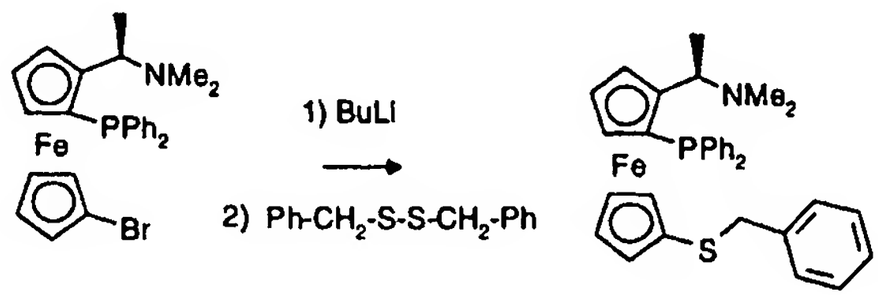
Example 15:



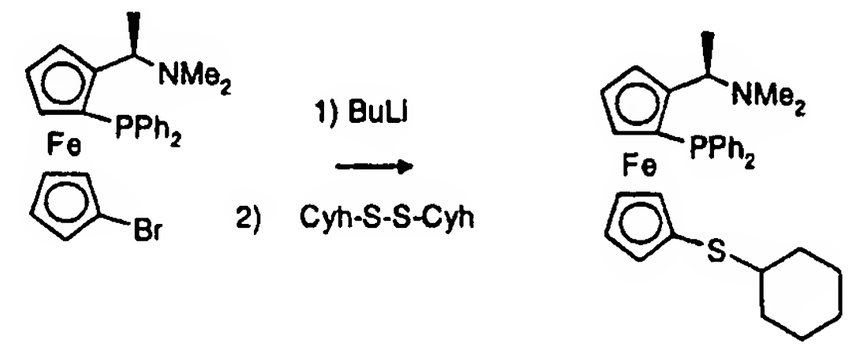
(4) (112)

0.83 ml (1.3 mmol) of BuLi is added dropwise at -40°C over a period of 30 minutes to a solution of 626 mg (1.2 mmol) of compound (4) in 10 ml of diethyl ether, and the mixture is stirred at that temperature for a further 30 minutes. The mixture is then cooled to -78°C and 341 mg (1.56 mmol) of phenyl disulfide are added, cooling is removed and the mixture is stirred overnight. Saturated sodium hydrogen carbonate solution is then added to the reaction mixture and extraction is carried out 3 times with ethyl acetate. The combined organic phases are washed with saturated NaCl solution, dried over sodium sulfate, concentrated by rotary evaporation and purified by chromatography (silica gel: Merck 60; eluant: hexane/ethyl acetate 2:1 with 1% triethylamine). 568 mg of product are obtained (yield 86%, red oil).

Example 16:



(4) (17)



(4) (18)

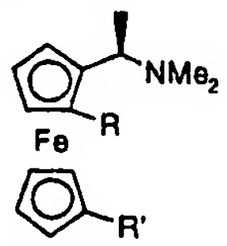
Compound (17):

(17) is prepared analogously to (11) starting from 0.48 mmol of (4) and 0.64 mmol of dibenzyl disulfide (duration of the reaction 12 hours). The crude product is extracted in water/ethyl acetate and purified by chromatography (eluant: ethyl acetate). Yield: 70% (orange, almost solid oil)

Compound (18):

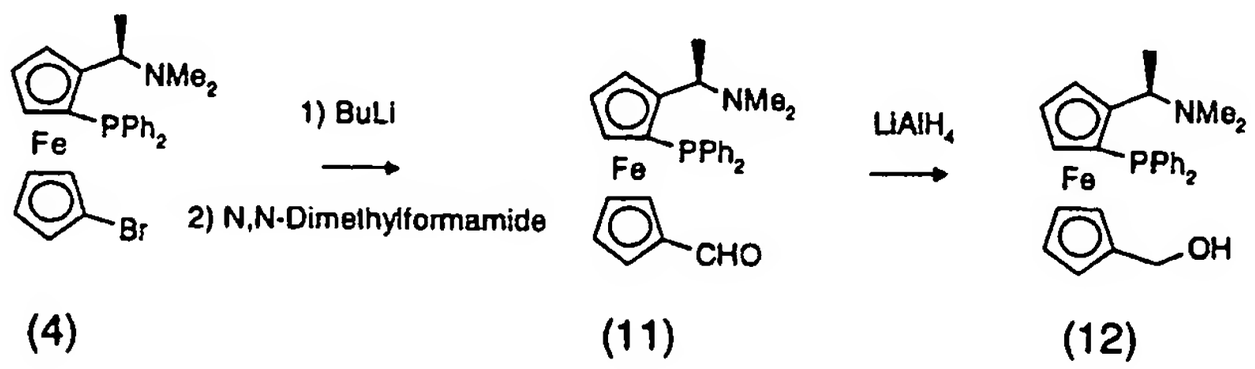
(18) is prepared analogously to (17). Purification by chromatography (eluant: hexane/ethyl acetate 1 : 1) yields the product in a yield of 86% (orange, almost solid oil).

Characteristic NMR signals of compounds containing sulfur:



Comp No.	R	R'	^{1}H-NMR (δ)	^{31}P-NMR (δ)
(10)	S-Ph	Br	7.00 - 7.25 (m, 5H, SPh)	-
(111)	S-Ph	PPh_2	6.95 - 7.20 (m, 5H, SPh) 7.20 -7.45 (m, 10H, PPh_2)	- 18.3
(113)	S-Ph	$P(Cyh)_2$	0.9 - 1.4 (m, $PCyh_2$) 6.95 - 7.20 (m, 5H, SPh)	- 8.66
(112)	PPh_2	S-Ph	1.38 (d, 3H, J=7, CH-C<u>H</u>$_3$) 6.95 - 7.55 (m, 15H, SPh and PPh_2)	- 24.4
(17)	PPh_2	S-CH_2-Ph	3.66 (s, 2H, CH_2-Ph)	- 22.6
(18)	PPh_2	S-Cyh	2.5 (m, 1H, S-CH)	- 22.4

Example 17:



(4) (11) (12)

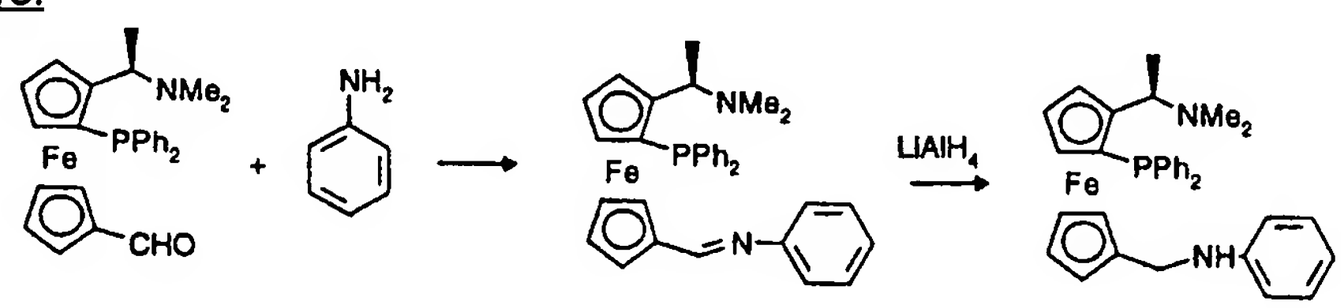
Compound (11):

1.3 Equivalents of a 1.6M solution of n-butyllithium in hexane are added dropwise at approximately -40°C to a solution of 2.88 mmol of (4) in diethyl ether (10 ml per mmol of (4)), and the mixture is stirred at that temperature for a further 30 minutes. The reaction with 2.8 mmol of N,N-dimethylformamide is carried out at -78°C. The reaction mixture is then stirred at 25°C for 4 hours, concentrated by rotary evaporation and extracted in toluene/water. The organic phase is dried with sodium sulfate and concentrated by rotary evaporation, and the crude product is purified by chromatography (silica gel Merck 60, eluant: hexane/ethyl acetate 1:1). Yield 84% (red, viscous oil).

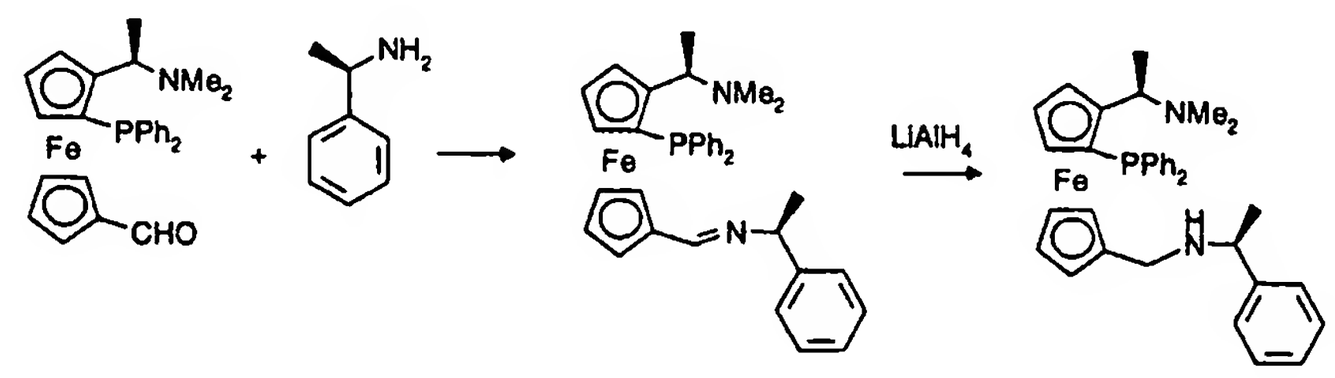
Compound (12):

A mixture of 0.46 mmol of (11) in diethyl ether (10 ml per mmol of starting material) and 1.9 mmol of lithium aluminium hydride is stirred at room temperature for 2 hours. There are then added first 0.2 ml of water and, once the evolution of hydrogen has subsided, diethyl ether and sodium sulfate, the mixture is filtered, the solution is concentrated by rotary evaporation and the crude product is purified by chromatography (eluant: ethanol). Yield 80% (red viscous oil).

Example 18:



(11) (13) (14)



(11) (15) (16)

Compound (13):

A mixture of 0.53 mmol of (11), 0.56 mmol of aniline and 0.5 g of molecular sieves is stirred in 3 ml of toluene at room temperature for approximately 20 hours. The mixture is then filtered, the molecular sieves are washed with a small amount of methylene chloride and the solution is concentrated by rotary evaporation. A viscous red oil is obtained in quantitative yield.

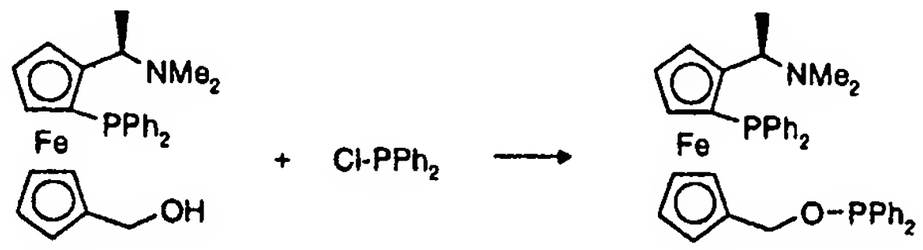
Compound (14):

0.24 mmol of (13) is reduced with 1 mmol of lithium aluminium hydride as described for (12). Purification by chromatography (eluant: EtOH) yields the product in a 90% yield (yellow, solid).

Compounds (15) and (16):

(15) is prepared analogously to (13) with S-2-phenylethylamine and (16) is prepared analogously to (15). Yield (16): 89% (yellow, solid)

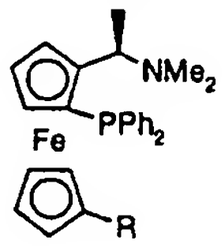
Example 19:



(12) (19)

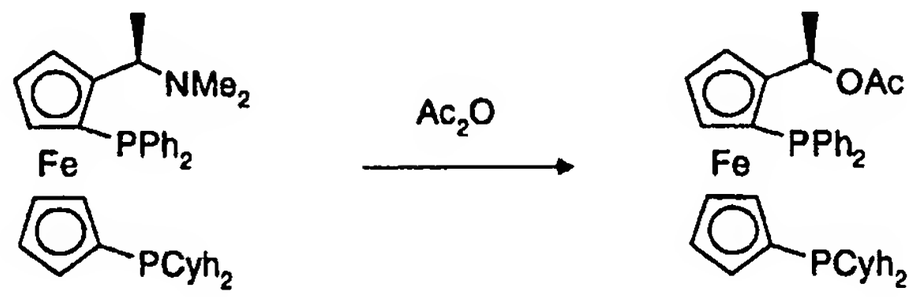
0.27 mmol of chloro-diphenylphosphine is added dropwise at 50°C to 0.22 mmol of (12) and 0.34 mmol of triethylamine in 3 ml of toluene. After 2 hours' stirring, the mixture is allowed to cool and the resulting cloudy orange mixture is purified by chromatography (eluant: ethyl acetate/triethylamine 100 :1). The product is obtained in a yield of 52% (yellow-orange, almost solid).

Characteristic NMR signals of compounds (11) to (16) and (19):



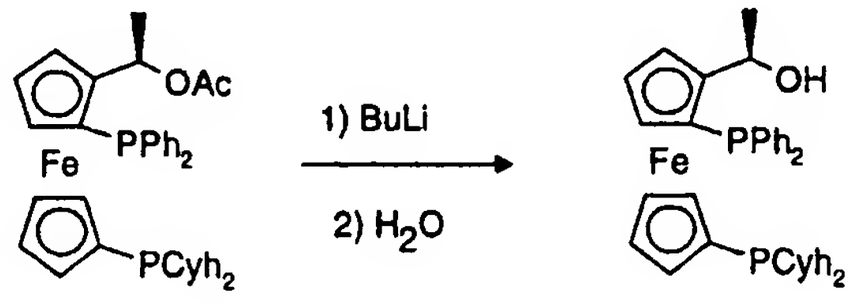
Comp No.	R	^{1}H-NMR (δ)	^{31}P-NMR (δ)
(11)	CHO	9.54 (s, 1H, CHO)	- 23.2
(12)	CH_2OH	3.96 - 4.08 (d of d, 2H, CH_2OH)	- 22.3
(13)	CH=N-Ph	7.92 (s, 1H, CH=N)	- 22.6
(14)	CH_2-NH-Ph	3.52 - 3.67 (d of d, 2H, C<u>H</u>$_2$-NH)	- 22.4
(15)	CH=N-CH(CH_3)Ph	1.50 (d, 3H, N-CH(C<u>H</u>$_3$)Ph)	- 22.5
		7.76 (s, 1H, CH=N)	
(16)	CH_2-NH-CH(CH_3)Ph	1.26 (d, 3H, N-CH(C<u>H</u>$_3$)Ph)	- 22.2
		2.9 - 3.16 (d of d, 2H, C<u>H</u>$_2$-NH)	
(19)	CH_2-O-PPh_2		- 22.2 (cp-PPh_2)
			+ 113.7 (O-PPh_2)

<u>Example 20:</u>



(100) (200a)

A solution of 206 mg (0.32 mmol) of (100) in 8 ml of acetic anhydride is stirred at room temperature for 24 hours. The orange solution is then extracted by shaking in aqueous NaCl solution and toluene, and the organic phase is washed with NaCl solution, dried over sodium sulfate and concentrated by rotary evaporation. 210 mg of crude product are obtained (orange almost solid oil), which is reacted further without purification.
^{1}H-NMR ($CDCl_3$) characteristic signals: δ 1.15 (s, C(O)CH_3), 6.19 (m, 1H, C<u>H</u>(CH_3)OAc.



(200a) (200)

0.5 ml of a 1.6M BuLi solution in hexane is added dropwise with stirring at 0°C to a mixture of 200 mg of the crude product (200a) in 10 ml of ether, and the mixture is stirred further for 2.5 hours at 0°C. At 0°C, 20 ml of water are then added to the mixture and extraction is carried out with ether. The organic phase is dried with sodium sulfate, concentrated by rotary evaporation and purified by chromatography (silica gel: Merck 60; eluant: ethyl acetate/hexane 1/2). 55 mg of product are obtained (yield 27% based on (100), viscous orange oil).

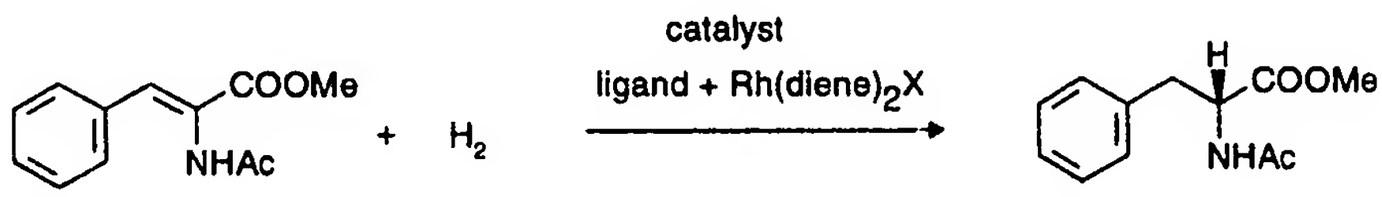
Analysis:

^{1}H-NMR ($CDCl_3$) characteristic signals: δ 1.48 (d, 3H, C-CH_3), 3.7-4.5 (m, 7H, $C_5H_3FeC_5H_4$), 4.95 (m, 1H, C<u>H</u>-CH_3), 7.2-7.6 (m, 10H, $P(C_6H_5)_2$.

^{31}P-NMR ($CDCl_3$): δ -7.1, -22.9

<u>Application Examples:</u>

<u>Hydrogenation of acetamidocinnamic acid methyl ester:</u>



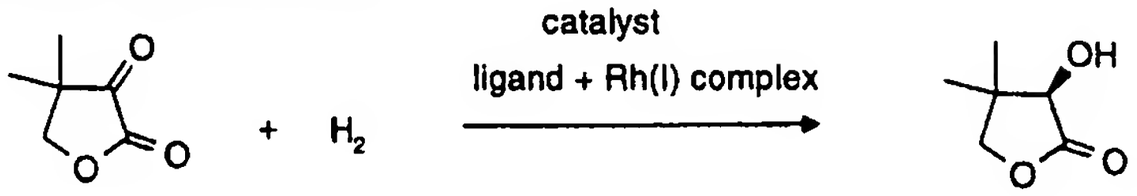
General: All the operations are carried out under inert gas. The hydrogenations are carried out in a 25 ml glass flask equipped with a magnetic stirrer (1500 rpm), an inert gas connection and a rubber septum. The reactants and the hydrogen are introduced using syringes and needles. All hydrogenations are carried out under normal hydrogen pressure.
Procedure: 0.018 mmol of ligand and 0.015 mmol of $[Rh(diene)_2]X$ are dissolved in 3 ml of MeOH in the hydrogenation vessel equipped with a magnetic stirrer and the solution is stirred for 10 minutes. To that catalyst precursor there is then added a solution of 1.5 mmol of acetamidocinnamic acid methyl ester in 7 ml of MeOH. Prior to each hydrogenation the inert gas in the hydrogenation vessel is displaced by hydrogen in 4 cycles (vacuum, normal hydrogen pressure). Hydrogenation is started by switching on the stirrer. The conversion is determined in each case by the consumption of hydrogen or by means of GC (column OV 101) and the optical yield is determined by means of GC (column: Chiracil-val). The results are given in the following Table:

Table 4:

Example No.	Ligand	Conf. of ligand	$Rh(diene)_2X$	Conversion [%]	Time [h]	ee	Conf. of product
30	(111)	S,R	$Rh(COD)_2BF_4$	83	6*	44	S
31	(113)	S,R	$Rh(COD)_2BF_4$	98	7*	24	S
32	(15)	S,R	$RH(NBD)_2BF_4$	90	21	16	R
33	(103)	R,S	$Rh(NBD)_2BF_4$	83	16	83	R
34	(103)	R,S	$Rh(COD)_2BF_4$	100	0.8*	79	R
35	(102)	S,R	$Rh(COD)_2BF_4$	100	5	76	S
36	(13)	S,R	$Rh(NBD)_2BF_4$	95	24	52	R
37	(14)	S,R	$Rh(NBD)_2BF_4$	66	19	71	R
38	(16)	S,R	$Rh(NBD)_2BF_4$	77	25	67	R
39	(17)	S,R	$Rh(NBD)_2BF_4$	88	18	49	R
40	(18)	S,R	$Rh(NBD)_2BF_4$	95	22	62.5	R

* Addition of 10 microliters of $MeSO_3H$ before the hydrogenation

Hydrogenation of keto-pantolactone:

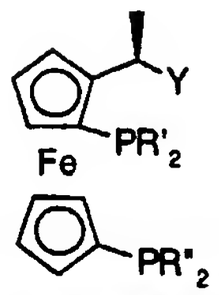


General: All the operations are carried out under inert gas. The hydrogenations are carried out in a 50 ml steel autoclave equipped with a magnetic stirrer (1500 rpm). The reactants and the hydrogen are introduced using syringes and needles. All hydrogenations are carried out at 50 bar hydrogen pressure.

Procedure: 0.0096 mmol of ligand and 0.008 mmol of Rh(I) complex are dissolved in 3 ml of solvent in a vessel equipped with a magnetic stirrer and the solution is stirred for 10 minutes. The solution is introduced into the autoclave against a current of argon. To that catalyst precursor there is then added a solution of 4 mmol of ketopantolactone in 5 ml of solvent. Prior to each hydrogenation the inert gas in the autoclave is displaced by hydrogen in 4 cycles (vacuum, normal hydrogen pressure). Hydrogenation is started by switching on the stirrer and terminated after 20 hours. The conversion and the optical yield are

determined by means of GC (columns: OV 101, Lipodex-E). The results are given in the following Table 5:

Table 5:

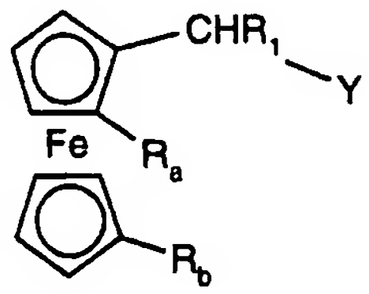


Ex. No.	Ligand	R'	R"	Conf.	Rh(I) complex	T °C	Sol-vent	Conv-ersion	ee	Conf.
41	100	Ph	Cyh	R,S	$[Rh(COD)Cl]_2$	50	THF	98	77	S
42	101	Ph	Cyp	R,S	$[Rh(COD)Cl]_2$	50	THF	100	65	S
43	109	o-Tol	Cyh	S,R	$[Rh(COD)Cl]_2$	50	THF	100	72	R
44	109	o-Tol	Cyh	S,R	$[Rh(NBD)OAc]_2$	50	THF	100	75	R
45	109	o-Tol	Cyh	S,R	$[Rh(NBD)OAc]_2$	50	Tol	100	81	R
46	109	o-Tol	Cyh	S,R	$[Rh(NBD)OAc]_2$	25	Tol	100	84	R
47	105	p-$PhCF_3$	Cyh	R,S	$[Rh(COD)Cl]_2$	50	THF	95	67	S
48	200	Ph	Cyh	R,S	$[Rh(COD)Cl]_2$	50	THF	100	65	S

Y is NMe_2 in Ex. No. 41 to 47 and Y is OH in Ex. No. 48

What is claimed is:

1. A compound of formula



(I), wherein

R_1 is C_1-C_8alkyl, C_5-C_{12}cycloalkyl, phenyl or phenyl substituted by from 1 to 3 substituents selected from C_1-C_4alkyl and C_1-C_4alkoxy;

R_a is $-P(R_{10}R_{11})$ or $-SR_{12}$;

R_b is $-P(R'_{10}R'_{11})$, $-SR'_{12}$, $-CH=NR_{12}$, $-CH_2-NH-R_{12}$ or $-CH_2-O-P(R_{10}R_{11})$;

R_{10} and R_{11} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl; or

R_{10} and R_{11} together are C_4-C_8alkylene, C_4-C_8alkylene substituted by C_1-C_4alkyl or by phenyl, or annelated C_4-C_8alkylene;

R'_{10} and R'_{11} are each independently of the other as defined for R_{10} and R_{11} , with the proviso that $-P(R_{10}R_{11})$ is not identical to $-P(R'_{10}R'_{11})$;

R_{12} is H, C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;

R'_{12} is as defined for R_{12} , with the proviso that $-SR_{12}$ is not identical to $-SR'_{12}$;

R_4, R_5 and R_6 are each independently of the others C_1-C_{12}alkyl or phenyl;

R_7 and R_8 are each independently of the other H, C_1-C_{12}alkyl or phenyl, or

R_7 and R_8 together are tetramethylene, pentamethylene or 3-oxa-1,5-pentylene,

R_9 is H or C_1-C_4alkyl;

M is H or an alkali metal;

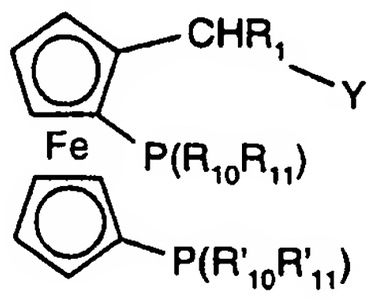
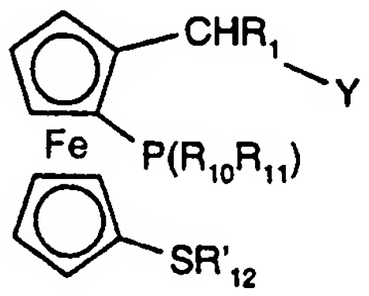
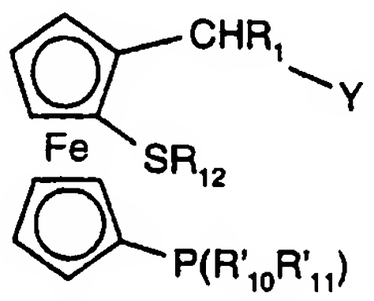
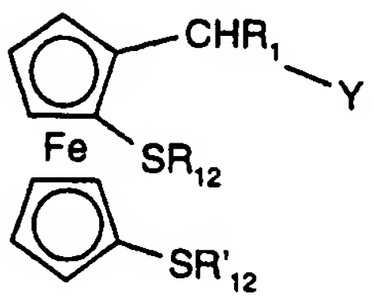
X^- is the anion of an acid;

Y is $-OR_{13}$, $-SR_{14}$ or $-NR_{15}R_{16}$;

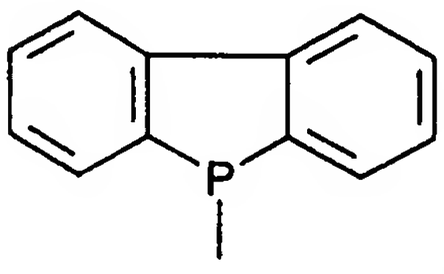
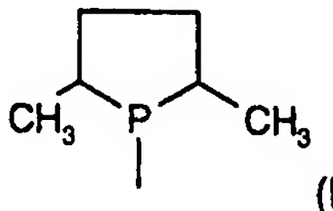
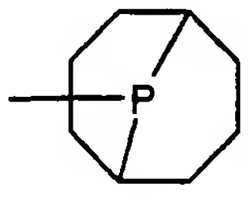
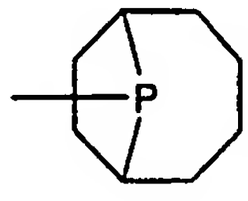
R_{13} is H, C_1-C_{18}alkyl, $-C(O)-C_{1-8}$alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$,

$-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R_{14} is H, C_1-C_{18}alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4-alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5-fluoroalkyl; and
R_{15} and R_{16} are each independently of the other C_1-C_{18}alkyl that may be substituted and/or interrupted by one or more hetero atoms, arylenes or carbocycles; or
$-NR_{15}R_{16}$ is a cyclic amine.

2. A compound of formula (I) according to claim 1 that corresponds to one of the formulae (Ia), (Ib), (Ic) and (Id)


(Ia),

(Ib),

(Ic),

(Id).

3. A compound of formula (I) according to claim 1, wherein
R_{10} and R_{11} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl; or the group
$-P(R_{10}R_{11})$ is a radical of formula IV, IVa, IVb or IVc


(IV),

(IVa),

(IVb),

(IVc).

4. A compound of formula (I) according to claim 1, wherein R_{10}, R'_{10}, R_{11}, R'_{11}, R_{12} and R'_{12} are each independently of the others cycloalkyl having from 5 to 8 carbon atoms.

5. A compound of formula (I) according to claim 1, wherein R_{10}, R'_{10}, R_{11}, R'_{11}, R_{12} and R'_{12} are each independently of the others unsubstituted phenyl or phenyl substituted by 1 or 2 substituents.

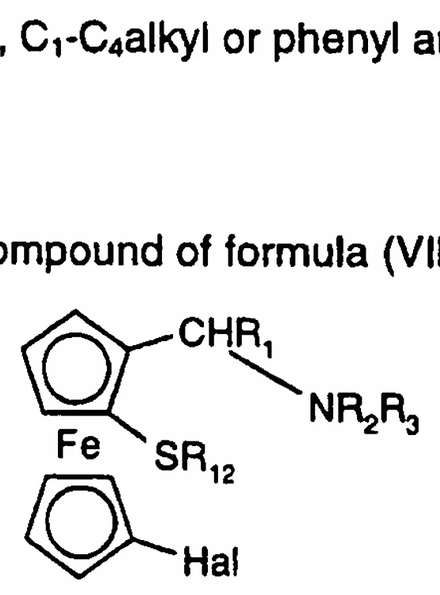
6. A compound of formula (I) according to claim 1, wherein R_{10}, R'_{10}, R_{11}, R'_{11}, R_{12} and R'_{12} are each independently of the others 2-methyl-, 3-methyl-, 4-methyl-, 2- or 4-ethyl-, 2- or 4-isopropyl-, 2- or 4-tert-butyl-, 2-methoxy-, 3-methoxy-, 4-methoxy-, 2- or 4-ethoxy-, 4-trimethylsilyl-, 2- or 4-fluoro-, 2,4-difluoro-, 2- or 4-chloro-, 2,4-dichloro-, 2,4-dimethyl-, 3,5-dimethyl-, 2-methoxy-4-methyl-, 3,5-dimethyl-4-methoxy-, 3,5-dimethyl-4-(dimethylamino)-, 2- or 4-amino-, 2- or 4-methylamino-, 2- or 4-(dimethylamino)-, 2- or 4-SO_3H-, 2- or 4-SO_3Na-, 2- or 4-[$^+NH_3Cl^-$]-, 3,4,5-trimethyl-, 2,4,6-trimethyl-, 4-trifluoromethyl- or 3,5-di-(trifluoromethyl)-phen-1-yl.

7. A compound of formula (I) according to claim 1, wherein R_{10}, R'_{10}, R_{11}, R'_{11}, R_{12} and R'_{12} are each independently of the others cyclohexyl, n-butyl, isobutyl, tert-butyl, phenyl, 2- or 4-methylphen-1-yl, 2- or 4-methoxyphen-1-yl, 2- or 4-(dimethylamino)phen-1-yl, 3,5-dimethyl-4-(dimethylamino)phen-1-yl or 3,5-dimethyl-4-methoxyphen-1-yl.

8. A compound of formula (I) according to claim 1, wherein Y is $-OR_{13}$ or $-NR_{15}R_{16}$.

9. A compound of formula (I) according to claim 1, wherein Y is $-OR_{13}$ or $-NR_{15}R_{16}$ in which R_{13} is H, C_1-C_4alkyl or phenyl and R_{15} and R_{16} are each independently of the other C_1-C_{18}-alkyl.

10. A compound of formula (VIb)



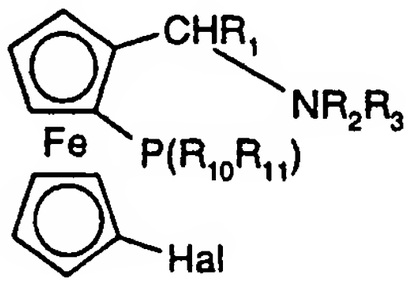
(VIb), wherein

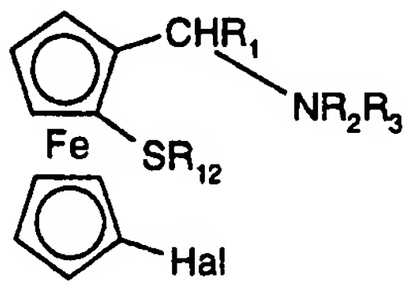
R_1 is C_1-C_8alkyl, C_5-C_{12}cycloalkyl, phenyl or phenyl substituted by from 1 to 3 substituents selected from C_1-C_4alkyl and C_1-C_4alkoxy;

R_2 and R_3 are each independently of the other hydrogen or C_1-C_{12}alkyl;

R_{12} is H, C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R_4, R_5 and R_6 are each independently of the others C_1-C_{12}alkyl or phenyl;
R_7 and R_8 are each independently of the other H, C_1-C_{12}alkyl or phenyl, or
R_7 and R_8 together are tetramethylene, pentamethylene or 3-oxa-1,5-pentylene,
R_9 is H or C_1-C_4alkyl;
M is H or an alkali metal;
X^- is the anion of an acid; and
Hal is F, Cl, Br or I.

11. A process for the preparation of a compound of formula (Ia), (Ib), (Ic) or (Id) according to claim 2, in which process
(a) in an inert organic solvent, alkyllithium is added to a compound of formula



(VIa) or


(VIb), wherein

R_1 is C_1-C_8alkyl, C_5-C_{12}cycloalkyl, phenyl or phenyl substituted by from 1 to 3 substituents selected from C_1-C_4alkyl and C_1-C_4alkoxy;
R_2 and R_3 are each independently of the other hydrogen or C_1-C_{12}alkyl;
Hal is F, Cl, Br or I;
R_{10} and R_{11} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl; or
R_{10} and R_{11} together are C_4-C_8alkylene, C_4-C_8alkylene substituted by C_1-C_4alkyl or by phenyl, or annelated C_4-C_8alkylene;
R_{12} is H, C_1-C_{12}alkyl, C_1-C_{12}alkyl substituted by C_1-C_4alkoxy, C_5-C_{12}cycloalkyl or by phenyl, C_5-C_{12}cycloalkyl, phenyl, C_5-C_{12}cycloalkyl substituted by C_1-C_4alkyl or by C_1-C_4alkoxy, or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R_4, R_5 and R_6 are each independently of the others C_1-C_{12}alkyl or phenyl;

R_7 and R_8 are each independently of the other H, C_1-C_{12}alkyl or phenyl, or
R_7 and R_8 together are tetramethylene, pentamethylene or 3-oxa-1,5-pentylene,
R_9 is H or C_1-C_4alkyl;
M is H or an alkali metal;
X^- is the anion of an acid;
and the mixture is caused to react; and
(b) either a compound of formula (VIa) or a compound of formula (VIb) is reacted with a compound of formula $R'_{12}SSR'_{12}$ (Vc) or $ClP(R'_{10}R'_{11})$ (Vd) in which R'_{10} and R'_{11} are each independently of the other as defined for R_{10} and R_{11} , with the proviso that $-P(R_{10}R_{11})$ is not identical to $-P(R'_{10}R'_{11})$, and R'_{12} is as defined for R_{12} with the proviso that R_{12} is not identical to R'_{12} ;
and optionally the radical $-NR_2R_3$ is converted into the radical -Y,
wherein Y is $-OR_{13}$, $-SR_{14}$ or $-NR_{15}R_{16}$;
R_{13} is H, C_1-C_{18}alkyl, -C(O)-C_{1-8}alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5fluoroalkyl;
R_{14} is H, C_1-C_{18}alkyl, phenyl or phenyl substituted by from one to three substituents selected from C_1-C_4alkyl, C_1-C_4-alkoxy, $-SiR_4R_5R_6$, halogen, $-SO_3M$, $-CO_2M$, $-PO_3M$, $-NR_7R_8$, $-[^+NR_7R_8R_9]X^-$ and C_1-C_5-fluoroalkyl; and
R_{15} and R_{16} are each independently of the other C_1-C_{18}alkyl that may be substituted and/or interrupted by one or more hetero atoms, arylenes or carbocycles; or
$-NR_{15}R_{16}$ is a cyclic amine.

12. A transition metal complex containing as ligand a compound of formula (I) according to claim 1.

13. A transition metal complex according to claim 12, wherein the transition metal is selected from the group Rh, Ir, Ru, Pd, Ni and Au.

14. The use of a compound of formula (I) according to claim 1 as ligand for transition metals in enantioselective catalysis.

15. The use according to claim 14 as ligand for rhodium or iridium in the catalytic hydrogenation of carbon/carbon or carbon/hetero atom double bonds.

INTERNATIONAL SEARCH REPORT

	ational Application No PCT/EP 97/05480

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F17/02 B01J31/28 C07B31/00 C07B53/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F B01J C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PASTOR, S.D. : "new chiral thio- and seleno-substituted ferrocenylamines" TETRAHEDRON, vol. 44, no. 10, 1988, pages 2883-2886, XP002051368 see the whole document ---	1-11
X	TOGNI, A. ET AL.: "chiral cooperativity: the nature of the diastereoselective and enantioselective step in the gold(I)-catalyzed aldol reaction utilizing chiral ferrocenylamine ligands" THE JOURNAL OF ORGANIC CHENISTRY, vol. 55, 1990, pages 1649-1664, XP002051369 see the whole document ---	1-13

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[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of theinternational search	Date of mailing of the international search report
7 January 1998	16/01/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rinkel, L

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PCT/EP 97/05480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	KNOX, G.R. ET AL.: "ferrocene derivatives. part xvi. the aminomethylation of methylthio- and bismethylthio-ferrocene" JOURNAL OF THE CHEMICAL SOCIETY (C), 1967, pages 1842-1847, XP002051370 see the whole document ---	1-11
X	BUTLER, I.R. ET AL.: "the synthesis of alpha-n,n-dimethyl-1'-diphenylphosphinofer rocenylethylamine and related ligands" CANADIAN JOURNAL OF CHEMISTRY, vol. 61, 1983, pages 147-153, XP002051371 see the whole document ---	1-11
X	NAIINI, A.A. ET AL.: "synthesis of new ferrocenyl amine sulfide and selenide complexes of group 10 metals and their catalytic activities toward selective hydrogenation, isomerization, and asymmetric grignard cross-coupling reactions" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 390, 1990, pages 73-90, XP002051372 see the whole document ---	1-15
X	CULLEN, W.R. ET AL.: "polymer supported ferrocene derivatives. catalytic hydrosilylation of olefins supported palladium and platinum complexes" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 333, 1987, pages 269-280, XP002051373 see the whole document ---	1-11
X	CHEMICAL ABSTRACTS, vol. 122, no. 11, 13 March 1995 Columbus, Ohio, US; abstract no. 133349e, ABBENHUIS, H.C.L. ET AL.: "a new stereoselective approach to chiral ferrocenyl ligan ds for asymmetric catalysis" XP002051374 see abstract & ORGANOMETALLICS, vol. 13, no. 11, 1994, pages 4481-4493, ---	1-11
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 112, no. 5, 29 January 1990 Columbus, Ohio, US; abstract no. 36097g, NAIINI, A.A. ET AL.: "synthesis and characterization of new ferrocenylamine sulfide and selenide complexes" XP002051375 see abstract & INORG. CHIM. ACTA, vol. 160, no. 2, 1989, pages 241-244,	1-11
X	CHEMICAL ABSTRACTS, vol. 113, no. 1, 2 July 1990 Columbus, Ohio, US; abstract no. 6550c, LAI, C.K. ET AL.: "new chiral ferrocenylamine sulfide and selenide ligands: preparation, characterization and their palladium and platinum complexes as catalysts for selective hydrogenation" XP002051376 see abstract & INORG. CHIM. ACTA, vol. 164, no. 2, 1989, pages 205-210, cited in the application	1-15

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